Photoluminescence of Single InAs Quantum Dots Obtained by Self-Organized Growth on GaAs

J.-Y. Marzin, J.-M. Gérard, A. Izraël, and D. Barrier

France Telecom, Centre National d'Etudes des Télécommunications–PAB, Laboratoire de Bagneux, BP107, F92225 Bagneux, France

G. Bastard

Laboratoire de Physique de la Matière Condensée, Ecole Normale Supérieure, 24 rue Lhomond, F75005 Paris, France

(Received 11 March 1994)

We present photoluminescence data on InAs quantum dots grown by molecular beam epitaxy on GaAs. Through the reduction of the number of emitting dots in small mesa structures, we evidence narrow lines in the spectra, each associated with a single InAs dot. Beyond the statistical analysis allowed by this technique, our results indicate short capture and relaxation times into the dots. This approach opens the route towards the detailed optical study of high quality easily fabricated single semiconductor quantum dots.

PACS numbers: 71.50.+t, 73.20.Dx, 78.55.Cr

Low dimensionality semiconductor structures constitute very attractive objects both for their fundamental properties and their potential applications in micro- and optoelectronics. While quantum well structures are already widely used in optoelectronic devices, quantum wires and quantum dots appear to be much more difficult to fabricate for this purpose [1]. Though the observations of low temperature photoluminescence (PL) on a single quantum dot [2] or of an isolated short wire [3] were recently reported, most results concern so far collections of objects with large fluctuations of sizes, which both restrains drastically the interest for applications and mask the influence of their intrinsic properties. In the case of quantum dots, besides the technological difficulties of their fabrication, fundamental limitations as the slowed down relaxation between confined states [4–8] were theoretically predicted. They are, however, difficult to study on an inhomogeneous collection of dots, while the fabrication and experiments on a single dot still constitute a challenge. In Ref. [2], the multiple lines detected in the PL spectrum of a single dot fabricated by local intermixing were interpreted in terms of emission from confined excited states. However, due to the fabrication process, the interpretation of the details of the PL spectra for various dot sizes appears to be very difficult. In this Letter, we demonstrate the validity of an alternative approach to observe high quality single InAs/GaAs quantum dots, similar in spirit to the methods used to study the optical properties of single molecules [9]. Because of the large calculated energy distance between confined levels, such single dots constitute ideal objects for studying relaxation phenomena.

It was indeed shown several years ago that the growth of a highly lattice mismatched semiconductor layer onto a substrate could lead to the spontaneous formation of semiconductor clusters with sizes in the quantum range. Such a situation was in particular observed in the InAs/GaAs [10–16] (7% mismatch) and InGaAs/GaAs systems [17,18]: When an InAs layer is deposited on a GaAs substrate, the growth is first obtained with a bidimensional (2D) mode and, beyond a limit of the order of 1.7 InAs [11,16] monolayer (ML), InAs islands are nucleated on the surface. If the growth is interrupted, these islands evolve and a quasiequilibrium is reached after typically 10 s [19]. This quasiequilibrium distribution could be studied by atomic force microscopy (AFM) [20]: The nucleated islands are small InAs square based pyramids (2.8 nm high, base dimension around 24 nm with a relative fluctuation of 15% for an InAs amount of 1.8 ML), laying on one 2D InAs layer. The typical center to center interisland distance is of the order of 55 nm. The angles of the pyramid merely depend on its size and correspond on the average to (410) limiting planes [20]. If the growth proceeds with GaAs deposition, one obtains InAs clusters which are free of nonradiative defects, as shown in previous studies [11]. These objects constitute local potential wells for electrons and holes and exhibit an efficient photoluminescence. From the point of view of their size and crystalline quality, these InAs clusters are ideal quantum dots and their size fluctuations are very small, as compared to the state of the art of artificial dots. We clearly evidence in the following the influence of the statistical distribution of their sizes on the PL, and observe for the first time the emission of single such quantum dots.

The samples were grown by molecular beam epitaxy at 520 °C. Sample A (B) consists of a (100) GaAs substrate onto which a 500 nm GaAs buffer layer was first deposited, followed by a 2.2 ML (1.7 ML) deposition of InAs, and a 100 nm GaAs cap layer. Both samples contain InAs clusters and are further processed using e^--beam lithography to remove the InAs clusters except in mesas. Those square mesas with a side of 5000, 2000, 1000, 500, 200, and 100 nm are insolated in polymethylmethacrylate using a JEOL 5DIIU machine, transferred to a Ni mask using a standard lift-off procedure and etched using $SiCl_4$ reactive ion etching. The distance between mesas is 15 μm.

0031-9007/94/73(5)/716(4)$06.00

© 1994 The American Physical Society

The cw photoluminescence spectra were obtained using a Ti sapphire tuneable laser, pumped by a Ar^+ ion laser. The laser beam is first cleaned by a prism monochromator and focused through a microscope objective onto the sample situated in a circulation He cryostat. The spot diameter is 2 μm and the power density around 1 kW/cm^2. The PL signal is collected through the same microscope objective, dispersed by a double 1 m focal length monochromator and detected by a photon counting system based upon an avalanche Si photodiode.

Figure 1 shows the 10 K PL spectrum of a 5000 nm mesa of sample A, with an excitation energy of 1.5 eV. This emission is typical of InAs clusters [11]. Its limited full width at half maximum (50 meV for both samples) results from a careful optimization of the growth conditions. It is attributed to an inhomogeneous distribution of cluster sizes and the emission line can be fitted by a Gaussian curve (standard deviation $\sigma = 25$ meV).

In order to calculate the dots' energy levels, we assume that GaAs overgrowth affects only the top InAs island monolayer through indium segregation effects, consistently with what was evidenced on 2D InAs/GaAs structures [21]. However, the size of the InAs islands is smaller than what is observed by AFM, due to the quenching of their evolution by the GaAs deposit. We nevertheless assume that they already have a pryamidal shape with the same base angle at the early stage of their formation, and this is our main approximation.

Figure 2 shows the low temperature calculated energies of the lowest energy transitions for the InAs clusters, in a simple effective mass treatment, of which a detailed presentation is beyond the scope of the present Letter. Basically, we approximate the pyramid by a cone of axis Z, with the same base surface and height. We include the effect of the indium segregation at the InAs/GaAs interface [21] during the GaAs overgrowth by spreading the top InAs ML with an $\exp(-Z/L)$ profile ($L = 1.1$ nm) and assuming for the In(Ga)As layer the same strain state as for the 2D case. This latter approximation is justified because the clusters have a very flat shape. Finally, the nonseparable Hamiltonian is diagonalized numerically for electrons, heavy holes, and light holes. The calculated transitions can be shown to be, for a given extension of

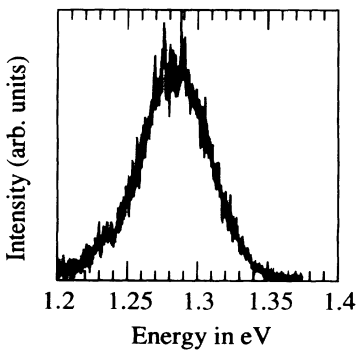

FIG. 1. 10 K PL spectrum of a 5000 nm mesa in sample A.

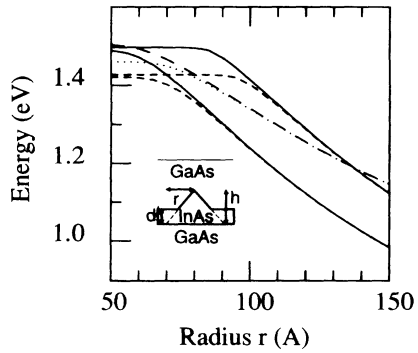

FIG. 2. Low temperature calculated fundamental and first excited transitions as a function of the radius r of the InAs cluster whose schematic structure is shown in the inset, for $d = 0.33$ nm (e-hh: —; e-lh: – –), $d = 0.66$ nm (e-hh: - - -; e-lh: · · ·) and a cone base angle of 12.4°.

the potential on the Z axis and a given InAs volume, quite insensitive to the detailed shape of the cluster. The calculation whose results are displayed in Fig. 2 was done assuming that the clusters are lying onto a 1 or 2 ML uniform InAs layer. Note that, as shown schematically in the inset of Fig. 2, the radius indicated on the abscissa takes into account this underlying layer, and that we refer to the geometry of the islands prior to the GaAs overgrowth. At low r values, the fundamental transition energy tends to the band gap energy of an InAs quantum well of thickness d. At larger r values ($r > 8$ nm), the first states are strongly localized in the central part of the clusters so that this transition energy does not depend on d. This will allow us to determine the dots' radii from their emission energies.

The calculated energies can be compared with experimental data for quasiequilibrium distributions of dots where the islands' radii (and shape) are known from AFM. Such dots grown with a 1.8 ML InAs deposit and a 20 s growth interrupt before GaAs overgrowth emit at 1.07 eV at 10 K. From Ref. [20], $r = 13.5$ nm for these islands so that the calculated first and second transition energies are, respectively, 1.06 and 1.211 eV. Besides validating our calculation, this result clearly indicates that the PL peak corresponds to the fundamental transition.

The comparison of the experimental emission energies of sample A (B) with the calculated values yields $r =$ 9.5 nm (8 nm) and $h = 2.1$ nm (1.8 nm). For these parameters, there is only one electron, one light hole, and one heavy hole level bound in the dot for $d = 2$ ML. For $d = 1$ ML, a second electron (and heavy hole) state is marginally bound in the dot. The standard deviation in r is 0.5 nm. This figure, significantly smaller than that deduced by AFM in the equilibrium case, is impressive when compared to state of the art artificial dots.

Figure 3(a) shows the typical PL spectra of a 500 nm mesa obtained on sample A. Whereas the spectrum displayed in Fig. 1 could be nicely fitted by a Gaussian, we resolve in this spectrum a forest of narrow lines.

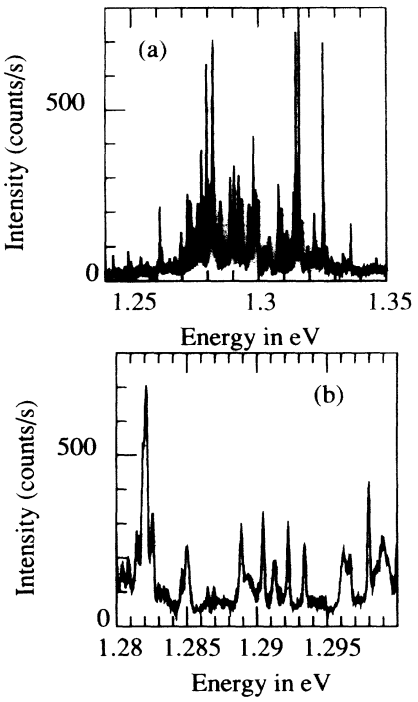

FIG. 3. (a) 10 K PL spectrum of a 500 nm mesa in sample A. (b) is a blow up of a part of the spectrum displayed in (a).

Figure 3(b) shows a blow up of this spectrum in a narrower energy range. The narrowest lines have a full width at half maximum smaller than the 0.1 meV resolution of our experimental setup. About 90 peaks can be counted in this particular spectrum. We checked carefully that the peaks positions are reproducible, independent of the laser energy, and change from one mesa to the other. We also studied on some of the more intense transitions the evolution of their energies with temperature between 5 and 90 K: They decrease with temperature, with variations intermediate between the very similar InAs and GaAs band gap dependences. Finally and contrarily to what is reported in Ref. [2], we cannot attribute several peaks to different optical transitions of a given cluster. All of them are indeed observed in a 80 meV energy range, smaller than the calculated energy separation between the first two transitions shown in Fig. 2. We therefore attribute each of these peaks to the emission of a specific InAs cluster. The evolution (not shown) between the spectra of 5000 nm mesa displayed in Fig. 1, in which the reproducible structures are already due to the limited number of emitting dots, to the spectrum of Fig. 3 is consistent with the reduction of the average number of transitions per unit energy as the total number of clusters in the studied mesa decreases.

In order to corroborate our interpretation, we have analyzed in detail the statistics of the peaks of the spectrum displayed in Fig. 3. Though there are large fluctuations of their intensities, the density of peaks per unit energy (regardless of their intensity), estimated by a floating average over 10 meV, reasonably follows the Gaussian curve deduced from the spectrum of Fig. 1, as can be seen in Fig. 4. Finally, on most 200 nm mesas of sample B, less than 10 peaks were observed as shown in Fig. 5. Figures 5(a)–5(c) are spectra obtained on different such mesas, whereas Fig. 5(d) was obtained by adding the spectra obtained on 20 different 200 nm mesas. This latter spectrum reproduces satisfactorily the typical density of peaks observed for larger mesas.

All these results are consistent with the assignment of the observed narrow transitions to PL lines each associated with a single cluster. These spectra also allow us to get a deeper insight into the cluster formation. As we observe about 100 peaks for a 500 nm mesa, we can deduce a typical surface occupied per cluster around $S = 50 \times 50\ \text{nm}^2$. This figure is very close to what is observed for "equilibrium" islands by AFM [20] so that the density of islands is likely to be fixed at the earliest times of their formation. This result suggests the following picture for the islands' formation: When evolving during a growth interrupt towards quasiequilibrium, the primary (quickly formed) islands grow in size at constant number at the expense of the 2D InAs layer. This is corroborated by the small variation (55 to 61 nm) of the interisland distance for a large increase of the InAs deposited amount (1.8 to 3.6 ML) reported in Ref. [20]. For sample A, where the InAs was deposited in 1 s and immediately overgrown by GaAs, the evolution of the islands is efficiently quenched when they are still in an early stage.

Knowing the size of the clusters (PL peak energy) and their density (number of peaks in a given mesa) which both do not depend on the average thickness d of the underlying 2D InAs layer, we can extract this latter parameter by writing the conservation of the total amount of InAs. It would correspond to 2.1 ML for sample A. Unfortunately, this determination of the average value of d does not give us the spatial distribution of the underlying layer. AFM shows that the thickness of this film is inhomogeneous and corresponds to roughly 1 ML in the vicinity of "equilibrium" islands. The existence of this underlying InAs film explains the observation of

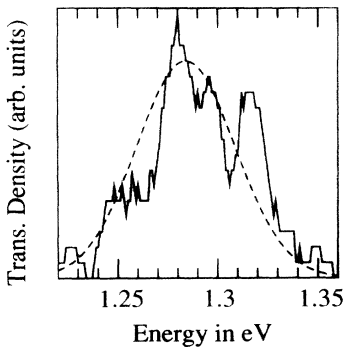

FIG. 4. Number of peaks per unit energy observed in the spectrum of Fig. 3 (full line) compared to the estimate from the Gaussian fit of the spectrum of Fig. 1 (broken line).

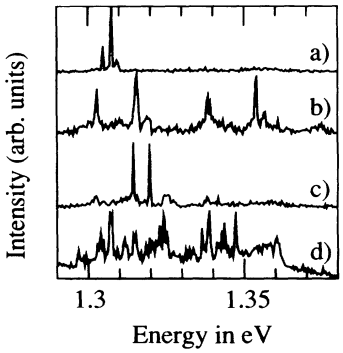

FIG. 5. (a), (b), and (c): 10 K PL spectra of three different 200 nm mesas of sample B. (d) sum of 20 spectra recorded on different such mesas.

intense PL signals with an excitation energy of 1.5 eV (used for all our experiments), below the GaAs band gap. This energy is above the fundamental transition energies calculated for 1 and 2 ML thick InAs quantum well in GaAs: Most carriers are created in a quasi-2D InAs layer and are further captured into the clusters. By varying the laser energy from 1.45 to 1.52 eV, we observed that the onset of PL of the individual lines observed in the spectrum of sample A is around 1.46 eV, closer to the gap of a 1 ML InAs quantum well. While the fundamental levels are not sensitive to the local environment of this InAs film, the first excited levels are, so that a more detailed microscopic study of the dot is necessary to know whether there are several bound states in those dots or not.

In any case ($d = 1$ or 2 ML), there is a calculated distance of at least 94 meV (54 meV) between the lowest electron (heavy hole) level and the first excited level for the average cluster of sample A. These figures are much larger than the longitudinal optical (LO) phonon energy in GaAs (36 meV). At the present time, the existing theoretical models [4–8] fail to explain the high PL efficiencies and short PL rise times [19] (in unprocessed samples) which we observe.

To summarize, we have observed the low temperature PL of single InAs clusters embedded in GaAs in samples where small mesa structures were designed by nanolithography. The statistics of the energies of these emissions in such small mesas are consistent with the spectra observed on unprocessed samples or large mesas. From the comparison with our calculations, we deduce a very homogeneous distribution of cluster sizes, as compared to state of the art artificial fabrication techniques, and get new insight into the formation of InAs clusters. These objects constitute very attractive test systems for the electronic properties of quantum dots because of their relatively easy fabrication, of their intrinsic regularity of size and of the large spacing between electronic levels as compared to room temperature thermal energy and to the LO phonon energy. Beyond these first observations, numerous additional experiments are still to be performed on these single semiconductor quantum dots. Among those, it will be important to check experimentally the microscopic structure of the dots and to detect by PL excitation the transitions between excited levels, if any. Finally, time resolved experiments on larger clusters with several bound electron and hole levels should allow us to deepen our understanding of energy relaxation in quantum dots.

The authors gratefully acknowledge J. M. Moison, R. Raj, B. Jusserand, F. Laruelle, and M. Voos for their fruitful comments and L. Ferlazzo for the etching of the mesa structures. Part of this work was partly supported by NANOPT EEC ESPRIT Basic Research Action.

[1] For a review of quantum wires and dots fabrication techniques and optical studies see K. Kash, J. Lumin **46**, 69 (1990).
[2] K. Brunner, U. Bockelmann, G. Abstreiter, M. Walther, G. Bohm, G. Trankle, and G. Weimann, Phys. Rev. Lett. **69**, 3216 (1992).
[3] L. Birotheau, A. Izraël, J. Y. Marzin, R. Azoulay, V. Thierry-Mieg, and F. R. Ladan, Appl. Phys. Lett. **61**, 3023 (1992).
[4] U. Bockelmann and G. Bastard, Phys. Rev. B **42**, 8947 (1990).
[5] H. Benisty, C. M. Sottomayor-Torres, and C. Weisbuch, Phys. Rev. B **44**, 10 945 (1991).
[6] T. Inoshita and H. Sakaki, Phys. Rev. B **46**, 7260 (1992).
[7] U. Bockelmann and T. Egeler, Phys. Rev. B **46**, 15 574 (1992).
[8] U. Bockelmann, Phys. Rev. B **48**, 17 637 (1993).
[9] Th. Basché, W. E. Moerner, M. Orrit, and H. Talon, Phys. Rev. Lett. **69**, 1516 (1992).
[10] W. J. Schaffer, M. D. Lind, S. P. Kowalczyk, and R. W. Grant, J. Vac. Sci. Technol. B **1**, 688 (1983).
[11] L. Goldstein, F. Glas, J. Y. Marzin, M. N. Charasse, and G. Le Roux, Appl. Phys. Lett. **47**, 1099 (1985).
[12] F. J. Grunthaner, M. Y. Yen, R. Fernandez, T. C. Lee, A. Madhukar, and B. F. Lewis, Appl. Phys. Lett. **46**, 983 (1985).
[13] F. Houzay, C. Guille, J. M. Moison, P. Henoc, and F. Barthe, J. Cryst. Growth **81**, 67 (1987).
[14] F. Glas, C. Guille, P. Henoc, and F. Houzay, Int. Phys. Conf. Ser. **87**, 71 (1987).
[15] O. Brandt, L. Tapfer, K. Ploog, R. Bierwolf, M. Hohenstein, F. Phillip, H. Lage, and A. Heberle, Phys. Rev. B **44**, 8043 (1991).
[16] J. M Gérard, Appl. Phys. Lett. **61**, 2096 (1992).
[17] C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander, Phys. Rev. Lett. **66**, 3032 (1991).
[18] D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Denbaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[19] J. M. Gérard, in "Confined Electrons and Photons: New Physics and Applications," edited by C. Weisbuch and E. Burstein, NATO ASI Series (Plenum, New York, to be published).
[20] J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatel, Appl. Phys. Lett. **64**, 196 (1994).
[21] J. M. Moison, C. Guille, F. Houzay, F. Barthe, and M. Van Rompay, Phys. Rev. B **40**, 6149 (1989).